

The Crystal Structure of Hydrazinium Trinitromethide, $(\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-)$ at $\sim -160^\circ\text{C}$

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The crystal structure of hydrazinium trinitromethide ($\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-$) has been determined using 1914 x-ray data collected photographically from a single crystal held at $\sim -160^\circ\text{C}$. The unit cell at $\sim -160^\circ\text{C}$ is $a = 7.91(2)$, $b = 11.77(2)$, $c = 13.98(2)$ Å, $\beta = 104.9(3)^\circ$, and contains eight formula weights in space group $\text{P}2_1/\text{n}$. The calculated density is $1.93 \text{ g}\cdot\text{cm}^{-3}$. The structure has been refined isotropically to $R = 0.10$ by full-matrix least-squares procedures. The two crystallographically independent trinitromethide anions are propeller shaped, with angles of 41° , 7° , 8° , and 74° , 5° , 4° , respectively, between the NO_2 and CN_3 plane normals. The central CN_3 part of each anion is almost planar. In one anion, the C atom is 0.008 Å out of the N_3 plane; in the other, the C atom is 0.033 Å out of the N_3 plane. Hydrogen atoms have been located approximately in an electron density difference synthesis. Their positions agree with those obtained from independent calculations involving the minimization of a function which is a first approximation to the electrostatic hydrogen bonding energy. These analyses provide evidence that one hydrazinium ion is eclipsed and the other is staggered.

Key words: Crystal structure; hydrazinium; hydrazinium trinitromethide; hydrogen bonding; trinitromethide; x-ray diffraction.

1. Introduction

The Hammett *para*-substituent constants [1]¹, the acid strengths [2], the ionization behavior [3], the equilibrium constants [4], and the strengths of the electron-withdrawing power in, but lack of resonance with, aromatic systems [5] have all provided evidence for the stability of the trinitromethide $[\text{C}(\text{NO}_2)_3]^-$ and tricyanomethide $[\text{C}(\text{CN})_3]^-$ anions and their derivatives. Such stability has been attributed to charge delocalization (i.e., resonance). The greater charge delocalization indicated in the tricyanomethide anion has suggested that while the tricyano anion is probably planar, the trinitromethide anion may not be so. To provide structural details on the trinitromethide anion, the structure of hydrazinium trinitromethide, $\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-$, has been determined. A preliminary report of the structure has been published [6].

2. Experimental Procedure

Needle-shaped crystals of $\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-$ were grown from an ethanol solution at about 2°C . Since the crystals decomposed within a few hours in the x-ray beam at room temperature, a single crystal 0.2 mm in diameter ($\mu_{\text{Mo}} = 3.2 \text{ cm}^{-1}$) was sealed in a borate glass capillary and cooled to $\sim -160^\circ\text{C}$ on a Weissenberg camera modified [7] to allow the routine collection of data at low temperatures. The unit cell was determined from Weissenberg and oscillation photographs to be* $a = 7.91(2)$, $b = 11.77(2)$, $c = 13.98(2)$ Å, $\beta = 104.9(3)^\circ$ (at $\sim -160^\circ\text{C}$) with space-group $\text{P}2_1/\text{n}$ and eight formula weights per cell. The equivalent positions are x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. The reciprocal lattice extinctions are $h0l$, $h+l=2n+1$; $0k0$, $k=2n+1$. The density was not determined directly but is calculated from the x-ray data to be $1.93 \text{ g}\cdot\text{cm}^{-3}$. X-ray data from 1914 reflections were collected photographically by the equi-inclination method for the levels $0 \rightarrow 7$, k, l , using molybdenum radiation, an 0.001 inch Nb filter and multiple films interleaved with $.0015$ inch brass sheets. The intensities of observed reflections

¹Figures in brackets indicate the literature references at the end of this paper.

*The digits in parentheses are estimates of the uncertainties in the least significant digit of the cell dimensions and are based on the standard errors of the measurements. They are compatible with experience with the technique. In the author's opinion, they may be considered to give an estimate of the standard deviations.

were estimated visually and corrected for the combined L_p and reflection size effects but not for absorption. The calculation of the quasi-normalized structure factors confirmed the centrosymmetry of the unit cell and gave initial values for the equi-inclination level scale factors. The equi-inclination levels were not scaled experimentally but the initial estimates agree with the final values from the full-matrix least-squares refinements within 5 percent on the average.

2.1. Determination of the Structure

One-hundred and six (106) phases were determined using a program by Chastain and Stewart [9, 10] which is an extension of the symbolic addition procedure [11, 12]. The structure was found from an E map calculated with these phases and from subsequent F_o Fourier syntheses. The structure was refined isotropically to $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.12$ using full-matrix least-squares procedures. The quantity minimized in the least-squares refinements is $\Sigma (w||F_o| - |F_c||)^2$. The weighting scheme used was 1 for reflections with $F_o \leq 6$ and $6/F_o$ for reflections with $F_o > 6$. The atomic scattering factors used are those of the neutral atoms. Those for C, N and O were taken from reference 13 and those for H from reference 14.

A difference electron density synthesis with coefficients weighted by the least-squares weights showed indications of the 10 hydrogen atoms of the hydrazinium ions. When the rest of the difference synthesis was examined, it was found that 8 of the peaks assigned to hydrogen were among the 12 highest peaks in the map. The peaks assigned to H(6) and H(7) were the 16th and 22nd highest peaks in the map but seemed to be relatively clearly defined in the map and in chemically reasonable positions. Of the 23 highest peaks, those not assigned to be hydrogen atoms were 0.36 to 0.75 Å away from the oxygens of the trinitromethide ions.

Hydrogen atoms were introduced at the positions suggested from the examination of the difference synthesis and the structure including the hydrogen positional parameters was refined isotropically to $R = 0.10$. Hydrogen thermal parameters were kept fixed at 2.0 Å². The effect of all reflections calculating over 60 was ignored in these least-squares refinements because

these reflections probably contained extinction and/or film scaling errors. No anisotropic refinement was attempted because of the correlation between the β_{11} thermal parameters and the level scale factors. Since the data were collected at $\sim -160^\circ\text{C}$, the thermal motion is expected to be relatively small, however.

The largest correlation coefficients are 0.3 between the scale factors, 0.3 between the scale factors and the atomic temperature factors and 0.4 between the temperature factors themselves. All other correlation coefficients are much less than 0.1.

The observed and calculated structure factors are compared in table 1 and the parameters of atoms other than hydrogen are given in table 2. The positions of the hydrogens from the weighted difference synthesis, the least-squares refinements, and from calculation (see later) are compared in table 3. The refinement changed the hydrogen positions obtained from the difference synthesis by an average of 0.17 Å. The average N-H distance thus changed from 0.86 Å to 0.89 Å. The location of covalently bonded hydrogen atoms by x-ray methods is known to be accompanied by a systematic error which makes the observed bond distance 0.1 to 0.2 Å shorter than the internuclear distance. The N-H distances observed here are therefore reasonable.

3. Description of the Structure

The crystal structure is shown in figure 1. There are two trinitromethide ions and two hydrazinium ions in the asymmetric unit. Each trinitromethide ion is propeller shaped with the plane of its N(1) nitrogroup twisted much more from the central CN₃ plane than are the planes of the other two nitrogroups. The central CN₃ part of each trinitromethide ion is essentially planar. One hydrazinium ion appears to be eclipsed (see figure 4); the other appears to be staggered (see figure 5).

The packing in the structure shows the following features. Anions of type 1 form a zigzag along the two-fold screw axis. The planes of neighboring anions are about 100° to one another. The zigzag results because adjacent anions are hydrogen bonded to the same hydrazinium ions. The O(15) . . . O(15) close approach of

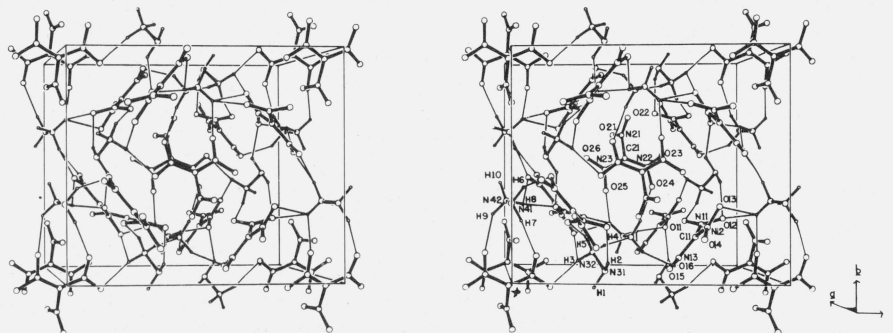


FIGURE 1. A stereoscopic view of the $\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-$ structure. The origin of the unit cell is denoted by *.

2.93 Å occurs when the zigzags come into close approach along the *c* axis.

The anions of type 2 are roughly equally spaced along the *a* axis with their centers almost on a straight line and with all atoms but O(21) and O(22) in a plane approximately parallel to the *bc* plane for a given anion.

The hydrazinium ions hold the anion 1 zigzags (along *a*) and anion 2 lines (along *b*) together in a three dimensional network. O(21) and O(22) in anion 2 are twisted almost perpendicular to the plane of the rest of the anion in order to squeeze between two anions of type 1.

4. Discussion

4.1. The Trinitromethide Ions

The bond distances and angles in the two propeller-shaped trinitromethide anions are given in table 4. The anions and their environments are shown in figures 1, 2, and 3. The central part C(N)₃ of anion 1 is essentially planar; C(11) is only 0.008(5) Å out of the (N)₃ plane. The central part of anion 2 is more distorted with C(21) 0.033(5) Å out of the (N)₃ plane. All but one of the N—O distances in the nitrogroups are within two standard deviations (~ 0.01 Å) of the average N—O distance, 1.232 Å. N(21)—O(22), the shortest at 1.214(4) Å, lies

out of this range. This may be related to weak or non-existent hydrogen bonding to O(22) (see sec. 4.2).

The dihedral angles between the normals to the planes of the nitrogroups and the normal to the best plane through the central CN₃ region of the anion are:

N(11) O(11) O(12):CN ₃	41°
N(12) O(13) O(14):CN ₃	7°
N(13) O(15) O(16):CN ₃	8°
N(21) O(21) O(22):CN ₃	74°
N(22) O(23) O(24):CN ₃	5°
N(23) O(25) O(26):CN ₃	4°

The intra-ionic O(21) . . . O(26) and O(22) . . . O(23) distances of 2.89 Å and 2.95 Å are much greater both than the corresponding intra-ionic distances in anion 1 (2.62, 2.57 Å) and than the other intramolecular O—O distances of 2.59, 2.65, 2.59, and 2.65 Å in both anions. These long distances allow the N(21) nitrogroup to be sandwiched between, and in approximate contact with, two anions of type 1 (figs. 1 and 3). The distances of closest approach between the N(21) nitro-

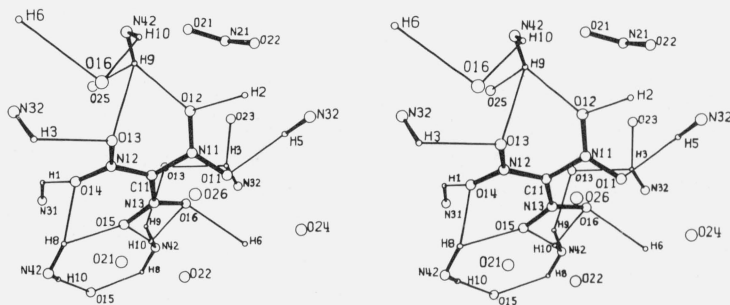


FIGURE 2. The environment of trinitromethide anion 1 (viewed perpendicular to the *ab* plane) showing the probable hydrogen bonding.

O . . . H distances ≤ 2.4 Å, other inter-atomic distances ≤ 3.1 Å are included.

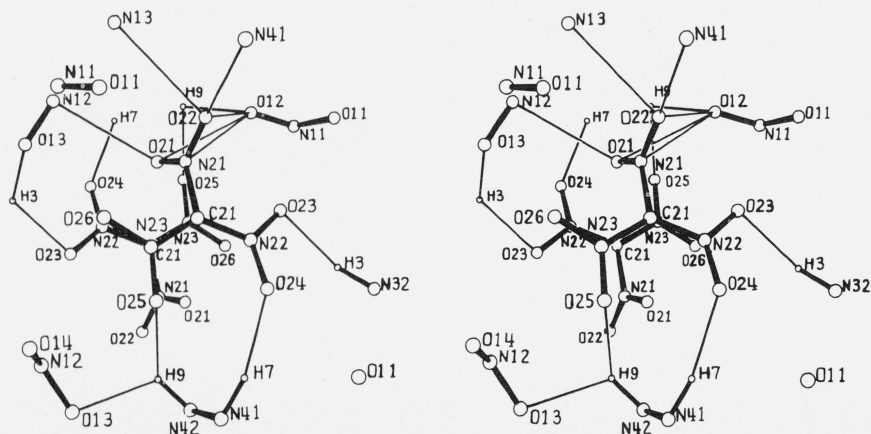


FIGURE 3. The environment of trinitromethide anion 2 (viewed perpendicular to the *bc* plane) showing the probable hydrogen bonding and possible van der Waals bonding to atoms 2.7–3.0 Å away from atoms in anion 2.

Otherwise as for figure 2.

TABLE 1. Observed and calculated structure factors^a for N₂H₅⁺ [C(NO₂)₃]⁻ (Columns are *l*, 10F_o, 10F_c)

0,0,L	10	137	-146	1,5,L	-1	223	212	-1	8041E-1394	2,7,L	8	325	258	-12	117	-127	5	256	262							
	11	185	176		0	95	-90	0	1001E-1379		8	355	258	-12	117	-127	5	256	262							
4	72	77	13	85	108	-16	58	41	1	56	47	1	272	-289	-15	57	69									
6	810E	720				-15	37	42	2	245	256	2	1168E	1223	-14	36	54	2,13,L	-10	88	104	8	150	137		
8	461	431	1,0,L			-13	291	244	3	156	265	-13	171	-87					-9	258	-120	9	51	44		
10	500	480				-11	1246	1304	4	164	129	5	180	163	-12	247	-233	-7	62	80	-7	264	-240	11	63	-79
12	561	448	-15	66	-57	-9	411	404	5	213	-118	6	168	-172	-10	142	143	-6	124	139	-6	124	139	-6	124	139
14	197	194	-9	130	121	-8	376	343	6	279	281	-8	94	109	-8	94	109	-8	94	109	-8	94	109	-8	94	109
16	188	144	-5	525E	-602	-7	140E	72	8	120	-97	8	417	394	-8	239	192	-8	239	192	-8	239	192	-8	239	192
	7	302	125	-6	739E	708	11	56	-55	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	
0,1,L	1	580E	579	-4	124	-145																				
	3	192	-213	-3	279	-268																				
2	350	-264	5	180	186	-2	235	-239																		
3	640	606	6	187	167	-11	32	-29	-11	32	-29	-11	32	-29	-11	32	-29	-11	32	-29	-11	32	-29	-11	32	
4	120	128	7	339	186	1	121	-143	-8	60	-64															
5	341	-298	9	585	543	3	74	-77	-7	260	200	2,3,L	0	93	-107											
6	580	-441	11	160	159	5	353	361	-6	87	93															
8	242	259	1	123	124	8	103	-105	-2	131	127	-15	73	72	3	69	56	-2	62	64	6	27	39	-3	87	
10	83	-124	1,1,L	8	134	-121	-1	112	-122	-14	166	149	4	231	-240	-1	48	46	7	260	-286	-2	230	-205	-1	
11	537	412																								
12	127	-114	-16	50	45	11	44	19	0	69	76	-13	203	-212	5	164	162	0	62	73	8	248	246	-1		
14	218	-227	-15	138	130	1	101	110	1	112	-112	-11	34	-45	7	75	-86	2	89	-87	10	299	-341	1	29	
16	148	-148	-12	48	-44	14	84	-70	5	270	231	-10	279	-229	8	180	-217									
			-11	256	-248				6	55	58	-9	92	98	10	93	88	3,0,L	12	166	175	2	346	-118		
0,2,L	-10	385	363	1,6,L					8	85	73	-7	23	16												
	0	156	-140	-8	373	-372	-15	115	-111	9	124	-131	-6	177	161	2,8,L	-17	95	82							
1	204	183	-7	199	226	-13	142	127	10	116	-90	-5	300	-237												
2	927E	708	-6	605E	-650	-12	297	253																		
3	221E	-178	-3	304	-330	-9	83	85	1,12,L	-2	563	-523	-12	326	-289	-14	91	74	-13	83	-86	-16	131	-103		
4	4211E	-3070	-3	304	-330	-9	83	85																		
5	436	-390	-2	287	196	-8	180	194	-10	99	-126	0	835E	-802	-9	209	-244	5	89	-95	-11	251	218			
6	183	-185	-1	199	173	-7	90	-99	-9	50	-47	1	21	-21	-8	204	1820	1	265	230	-10	247	214			
7	379	-348	1	234	-222	-14	246	-245	1	124	-102	2	392	-342	5	12	-12	3	666E	603	-7	94	109			
8	33	31	2	209	-185	-5	250	-237	-7	136	-128	3	161	-140	-6	216	228	5	345	340	-8	103	81			
9	229	-245	4	617E	630	-2	124	97	-5	175	173	4	304	296	-5	204	204	7	321	-322	-7	506	-477			
10	110	-135	5	747E	749	0	204	196	-3	158	153	5	288	290	-4	349	-365	9	114	131	-6	560	-484			
11	111	-116	6	202	-218	6	200	-212	-2	47	-112	2	362	349	0	320	-349	11	335	-382	-4	80	-54			
12	206	176	8	36	-32	3	113	-128	-1	102	-93	7	146	161	-2	37	-28									
13	206	-187	9	186	-162	4	61	-66	0	291	-250	8	273	-276	0	21	27	3,1,L	-3	281	-254	-7	101	111		
14	47	-33	10	148	146	5	89	73	1	50	63	50	1	26	-26											
16	104	-103	11	134	126	6	71	62	2	264	-264	7	131	-126	-13	105	-108	-14	108	104	-12	95	-95			
0,3,L	12	283	264			8	35	-29	5	48	39	13	127	124	5	154	-154	-12	195	-205	1	80	90			
						10	56	71	6	232	-200	6	75	-88	-11	146	-136	2	102	-92	-2	74	71			
1	425	-262	-15	37	-50	13	194	181	1,13,L	-13	176	-137	9	156	-166	-8	87	74	-13	83	-86	-16	131	-103		
2	920E	-575	-14	99	85	13	424	349																		
3	665	-590	-13	61	-72	14	198	-193	-7	67	70	-12	165	-263	10	185	-240	-6	245	-287	6	26	16			
4	5125E	814	-12	75	85	-5	79	72	-5	79	72	-5	79	72	-5	79	72	-5	79	72	-5	79	72	-5		
5	612	-457	-10	112	-117	-14	80	-83	-2	37	44	-9	363	-360	-13	115	108	-2	522	-424	11	120	-115			
6	346	-316	-9	113	-116	-14	80	-83	-2	37	44	-9	363	-360	-13	115	108	-2	522	-424	11	120	-115			
7	11263	-256	-8	44	-49	-13	45	-58	-1	143	-143	-7	146	-147	-10	35	36	-1	155	-153	12	97	110			
8	127	147	-7	147	-147	-10	134	-145	1	210	-196	-5	44	-147	-10	35	36	-1	155	-153	12	97	110			
9	148	-158	-6	752E	765	-10	134	-145	1	210	-196	-5	44	-147	-10	35	36	-1	155	-153	12	97	110			
16	40	-50	-5	169	194	-7	148	130	2	166	-151	-4	65	-64	-9	243	-203	2	250	-259						
0,4,L	-3	678E	-74	758E	771	-6	126	-116	3	135	-133	-3	34	-24	-8	28	-28	3	548	570	-15	43	41			
	-3	678E	-74	758E	771	-6	126	-116	3	135	-133	-3	34	-24	-8	28	-28	3	548	570	-15	43	41			
0	538	495	-1	595E	662	-3	174	-182	7	30	-28	-1	86	-81	-6	77	-62	6	397	415	-13	192	186			
1	61	-55	0	247	-255	-2	556	-573	1,14,L	1	41	-47	-3	102	-79	7	75	-55	-11	124	-144	-8	306	-269		
2	1026E	-856	1	253	-300	-1	64	-92																		
3	203	-214	3	45	-50	0	225	-236																		
4	62	-60	4	1482E	1649	2	95	85	-4	133	133	4	37	44	0	93	-88	11	128	-144	-8	306	-269			
5	301	306	5	102	-103	3	458	-480	-2	105	-75	2	245	235	1	30	-34	12	72	-68	-7	316	314			
6	121	-112	6	112	-122	5	161	-169	0	71	49	9	236	-211	3	178	-188	3,2,L	-5	171	-146	0	102	76		
7	128	109	7	261	272	5	51	56	0	71	49	9	236	-211	3	178	-188	3,2,L	-5	171	-146	0	102	76		
8	123	136	8	376	369	6	146	-160	1	165	-145	10	112	-106	5	76	-75	-16	162	155	-3	57	45			
9	156	174	9	258	-222	7	86	88	2	164	182	11	163	177	8	54	57	-13	166	163	-1	193	173			
16	52	-50	10	150	156	8	110	-111	4	66	78	13	119	-119	9	127	-107	-12	157	-156	0	197	-182			
0,5,L	11	65	12	150	156	11	65	44	2,0,L	2,5,L	11	37	23													
	13	57	50	14	51	54																				
2	156	-164	14	66	57	1,8,L	-14	111	-135	-16	165	204	2,10,L	-7	220	-206	4	229	-224	-9	53	78				
3	185	174				-12	175	-173	-15	76	-85															
4	94	102	1,3,L			-10	161	-207	-14	106	-97	-10	110	-100	-6	60	67	5	115	-127	-7	86	-72			
5	216	-208	-15	45	48	-82	113	188	-168	-8	516	-516	-7	10	42	-40										
6	306	324	-13	48	-55	-11	351	301	-6	60	56	-11	180	-182	-9	77	-74	-3	672E	-636	8	143	-159			
7	568	519	-12	93	99	-10	103	-117	-4	668E	732	-9	51	43	-8	1										

TABLE 1. Observed and calculated structure factors ^a for N₂H₅⁺ [C(NO₂)₂]⁻—Continued. (Columns are / · 10F_o, 10F_c)

4,1,L	1 73 73	2 192 208	-12 151 -140	-4 60 150	-4 161 152	-1 96 -108	3 94 98	1 58 58
4 28 -28	2 282 262	3 33 -16	-11 227 243	-3 33 -153	-2 173 -172	0 52 -56	2 61 61	2 61 61
5 76 89	4 125 -150	4 295 -306	-10 243 251	-2 70 73	-1 259 299	1 55 -42	3 37 57	3 37 57
6 104 -130	5 136 -151	5 53 -70	-9 174 187	0 49 -46	0 215 236	2 227 271	4 30 -32	4 30 -32
7 322 -320	6 44 41		-8 166 148	1 49 75	1 205 204	3 37 -20	5 139 -142	5 139 -142
8 185 216	7 183 209	4,11,L	-7 34 17	2 251 235	2 107 -101	4 214 254	-5 68 -65	6 60 63
9 118 121	10 237 239		-6 288 -294	3 265 -254	3 265 -341	5 194 217	-4 57 53	7 66 -85
10 73 -87	11 45 -50	-6 190 -169	-5 328 337	4 144 169	4 27 -29	6 22 -62	-3 26 45	8 91 89
11 113 107		-5 89 -95	-4 167 -132	5 110 109	5 67 -74	7 205 -202	-2 71 -71	
		-4 149 144	-3 328 361	6 100 -82	6 28 15	8 81 -82	-1 23 -16	7,5,L
		-2 249 218	-1 409 422	7 80 66	7 119 122	9 57 -59	0 17 15	
4,2,L		-1 101 -85	0 187 -188	8 100 102	8 90 -61		1 41 23	-13 165 -157
		0 89 91	1 65 55	9 81 116	9 72 62	6,6,L	2 30 39	-12 108 -94
-15 49 47	-13 50 -49	1 130 -111	2 134 -157					-11 26 13
-14 62 57	-12 165 146	2 35 -25	4 212 212	5,9,L	6,2,L	-14 68 56	7,0,L	-10 27 -29
-13 317 328	-10 62 38	4 74 -75	5 149 166			-13 70 -60		-9 441 -401
-12 200 179	-9 219 191		6 292 -329	-12 40 23	-16 71 -75	-11 106 -88	-13 167 -135	-8 350 296
-11 263 261	-8 108 -103	5,0,L	7 87 -105	-11 106 80	-15 89 82	-10 114 -76	-11 50 -47	-7 83 -57
-10 361 -331	-7 363 361		9 259 253	-10 61 -48	-14 224 -211	-9 51 38	-9 114 -97	-6 188 -177
-9 252 233	-6 312 -275	-15 196 -172	10 37 -39	-8 24 34	-13 47 41	-8 66 60	-7 169 -196	-5 147 -151
-8 305 257	-5 420 -386	-13 62 -48	11 66 -60	-7 24 41	-12 187 169	-7 304 281	-5 84 -80	-3 185 -195
-7 73 -75	-4 222 217	-11 289 310		-6 261 -239	-11 61 -54	-6 58 65	-1 654E 651	-2 164 -174
-6 540 -487	-3 321 303	-9 465 -468	5,5,L	-5 152 -160	-10 97 -93	-5 154 189	1 390 -353	-1 321 -362
-5 97 123	-2 94 95	-7 745E -727		-4 60 -53	-9 103 -119	-4 59 49	3 63 -56	0 72 -66
-4 287 242	-1 61 -54	-5 45 47	-15 240 261	-3 153 163	-8 77 61	-3 75 -91	5 111 89	1 319 -359
-3 746E 621	0 103 99	-3 263 -211	-14 65 64	-2 327 287	-7 93 73	-2 199 -218		2 141 158
-2 194 194	1 231 -219	1 173 -178	-12 277 227	0 173 -129	-6 104 115	-1 124 102	7,1,L	3 138 -154
-1 201 207	2 64 58	3 389 -172	11 288 243	-1 80 -82	-5 378 -344	0 21 9		5 132 -138
0 301 -270	4 228 -228	5 166 -150	-10 40 -21	2 111 -104	-4 122 100	1 126 118	-15 135 -122	7 78 -62
1 302 305	5 46 -42	7 178 -160	-9 116 120	3 308 259	-3 54 -45	3 163 204	-14 167 -156	
2 255 -266	6 33 -21		-8 59 -43	4 39 -33	-2 270 -309	4 164 -185	-13 38 -33	7,6,L
3 313 -328	7 50 -58	5,1,L	-7 421 388	5 26 23	-1 50 55	6 138 -119	-11 135 147	-13 66 -82
4 140 120	8 49 -63		-6 70 62	6 72 -71	0 269 351	7 213 206	-10 70 70	-12 20 -25
5 78 -78	9 78 -83	-16 84 84	-4 362 313	7 82 -88	1 335 -392	8 102 91	-9 153 -136	-11 22 31
6 155 -148	10 76 75	-15 119 119	-3 438 470	8 60 -74	2 48 -59	9 24 -40	-8 118 -107	-10 74 -92
7 93 97		-14 174 158	-2 37 -14		3 123 -152		-7 273 261	-9 64 74
8 93 99		-13 146 -124	-1 54 50	5,10,L	4 145 128	6,7,L	-6 148 -145	-8 183 -161
9 97 119		-12 21 26	0 297 294		5 137 -142		-5 74 -57	-7 116 98
11 156 166	-13 50 -55	-10 244 -207	1 119 -129	-11 16 -22	6 136 154	-12 77 -72	-4 111 107	-6 53 -42
4,3,L	-12 183 -147	-8 120 103	2 31 6	-9 41 32	7 100 82	-11 132 113	-3 327 304	-5 32 -33
	-10 61 63	-7 252 -265	3 348 411	-8 27 48	8 64 49	-10 222 195	-2 312 -285	-4 174 -215
-15 279 250	-9 204 -187	-6 98 77	4 131 -111	-7 309 317	10 43 -31	-9 251 250	-1 72 -72	-3 101 -108
-14 333 306	-8 288 -281	-5 101 -93	5 60 57	-5 93 82		-8 97 88	0 104 -104	-2 188 -207
-12 170 -167	-6 341 318	-3 343 320	6 66 64	-4 71 49	6,3,L	-7 229 187	1 85 85	-1 142 -136
-11 147 151	-5 75 89	-2 101 102	8 104 109	-3 77 91	-15 147 -139	-6 42 -42	2 340 326	0 145 163
-10 236 219	-4 157 -136	-1 169 214	9 227 233	-2 60 68	-14 102 -111	-4 114 111	7 60 43	2 339 -339
-8 318 297	-2 363 -336	1 155 -154	10 74 71	-1 108 112	-13 163 -160	-3 264 308		3 214 -208
-7 255 -216	-1 67 -67	2 143 -171	11 83 94	0 143 139	-12 123 102	-2 169 -188		4 103 -94
-6 236 -207	0 33 33	3 233 244		2 23 -27	-11 161 -165	-1 35 29	-15 87 104	7 76 -103
-5 296 -330	1 104 -108	4 103 -107	5,6,L	4 24 29	-10 201 213	0 30 16	-14 89 82	
-4 63 57	3 209 -215	5 239 -213	-14 44 51	5 49 -55	-9 238 -251	2 89 93	-12 177 -132	
-3 108 118	5 33 -13	6 112 119	-13 56 -45	6 31 31	-8 287 -313	3 142 166	-11 66 -68	7,7,L
-2 140 153	6 165 -172	7 76 84	-12 48 -50		-7 178 -137	4 177 156	-9 305 286	-12 81 -75
0 22 77	7 32 -41	8 222 246	-11 343 -294	5,11,L	-5 222 -211	6 84 69	-8 40 42	-11 251 -233
1 219 181	9 37 -75	9 255 256	-10 153 151		-4 156 135	7 85 68	-7 145 143	-10 83 61
2 159 140	11 58 -75		-9 272 -278	-8 453 468	-8 27 24	-3 381 -456	-5 378 -346	-9 41 19
3 171 -168		4,8,L	-7 81 -61	-6 90 94	-6 112 -101	-2 212 -212	-4 172 -170	-8 148 -118
4 124 -157		-16 60 -60	-5 481 -471	-5 52 -44	0 153 -183		-3 336 329	-7 104 95
5 32 -51	-11 241 203	-14 239 -204	-4 35 -32	-4 61 73	1 118 -98	-12 101 98	-2 49 -49	-6 50 35
6 34 -35	-9 245 215	-13 112 88	-3 62 61	-3 121 106	2 228 235	-11 70 -60	-1 183 -170	-5 45 40
7 35 40	-7 204 198	-12 140 144	-2 69 -45	-2 98 102	3 107 -101	-10 51 45	0 193 194	-4 158 -146
8 66 61	-6 126 129	-11 155 152	1 425 -466	-1 63 65	-4 44 -39	-9 169 -140	1 203 191	-3 32 13
9 81 94	-5 135 -95	-7 224 -224	2 265 280	0 99 101	5 156 -148	-8 66 -49	2 44 -32	-2 99 83
10 59 76	-3 486 464	-6 144 -157	3 94 -76	1 152 147	6 162 -179	-7 182 149	3 162 -162	-1 66 92
11 173 163	-2 97 88	-5 156 -148	4 150 160	2 77 -78	7 39 30	-6 98 76	4 106 -99	0 97 114
12 101 -112	-1 107 102	-3 605E 555	5 67 -55	4 74 60	9 203 -208	-5 220 -181	5 68 64	4 80 53
	0 155 139	-2 523 553	6 61 72	5 52 52	10 65 66	-3 320 -304	6 52 -48	5 100 127
4,4,L	1 73 -64	-1 116 137	7 164 153			-2 173 191	8 110 -112	6 69 80
-14 282 265	2 57 43	0 217 224	8 153 -134	5,12,L	6,4,L	-1 183 -204		
-13 195 -160	3 87 -80	2 142 122	9 148 -155	-7 30 -32	-15 27 34	1 150 98	7,3,L	7,8,L
-12 166 172	4 62 77	4 166 142	10 75 64	-6 25 29	-14 90 -81	2 158 -129	-14 84 -72	-10 35 21
-11 189 177	5 132 135	5 74 -62		-5 17 -5	-13 39 34	3 125 -122	-13 47 41	-9 44 -37
-10 210 235	6 96 -102	6 164 170		-4 17 -28	-12 334 -254	4 29 22	-12 63 35	-8 98 -92
-9 305 -272	8 65 70	8 39 -30		-3 231 -189	-11 235 -196	5 36 -34	-11 86 -75	-7 33 -42
-8 121 -103	10 62 -69	10 211 250	-14 127 123	-2 53 62	-10 91 -95	7 58 -72	-10 311 268	-6 99 90
-7 327 -311			-13 62 52	-1 47 -37	-9 81 59		-9 66 62	-5 43 30
-6 96 -98	4,9,L	5,3,L	-12 120E 78	0 101 -113	-8 36 -21	6,9,L	-8 77 92	-4 132 -137
-5 170 -188	-10 237 -204	-16 176 -174	-10 47 -36	1 43 40	-7 131 128		-6 343 311	-3 139 -116
-4 306 -279	-9 37 -60	-15 24 -23	-9 234 228	2 71 -90	-6 30 43	-11 145 -127	-5 359 359	-2 138 140
-3 120 -118	-8 68 72	-14 27 -9	-8 277 -239		-5 132 135	-8 184 145	-4 188 -179	-1 76 -58
-2 926E 852	-7 44 -27	-13 207 181	-7 38 -32	-6 79 -75	-4 344 -347	-7 206 -185	-3 115 -129	1 134 124
-1 470 456	-6 50 -33	-12 21 -26	-5 87 72	-14 147 -151	-2 128 -177	-6 38 18	-2 147 -159	3 94 70
0 150 160	-5 220 228	-11 227 -210	-3 114 -100	-12 27 -21	-1 171 175	-5 118 -123	-1 141 136	4 38 -51
1 306 -288	-4 126 109	-10 153 -156	-2 114 94	-10 162 144	0 142 -142	-4 221 -208	0 36 -30	7,9,L
2 315 -350	-3 62 48	-8 277 -243	-1 73 -54	-8 240 -274	3 227 -228	-2 82 85	4 243 204	-9 101 -116
3 186 -191	-1 87 -94	-7 271 -272	0 31 16	-6 142 131	5 228 278	-1 125 -127	6 327 -298	-7 100 91
4 286 279	1 33 8	-6 256 239	1 142 -151	-4 301 -322	6 66 72	1 237 -214	7 47 -61	-6 125 -96
5 70 -94	3 125 129	-4 230 -208	2 120 -126	-4 355 -335	7 111 95	3 26 -14	8 173 -168	-5 65 83
7 78 -83	4 244 -277	-3 126 142	3 114 122	2 277 -335	8 130 -107	4 95 81		-4 69 67
10 281 310	5 106 113	-1 96 99	4 35 15	4 238 -298	9 30 24	5 159 -163	7,4,L	-3 57 -59
11 51 50	7 63 64	0 44 68	5 151 171	6 28 -15	10 36 33			-1 73 100
12 35 44	8 166 182	1 28 13	6 34 -15	8 296 -314				0 46 57
4,5,L	9 28 -16	2 80 -86	7 237 -252	8 48 48	6,5,L	-9 170 208	-13 194 -169	1 125 136
	3 216 -271	4 35 -78	9 47 -44			-8 58 -68	-12 115 102	2 98 107
-15 42 -38	4,10,L	5 63 -78		6,1,L	-14 135 115	-7 67 29	-10 226 -220	7,10,L
-14 85 -83		7 76 70	5,8,L	-13 180 182	-12 124 104	-6 153 -136	-9 127 121	
-13 381 346	-9 46 28	10 44 51	-12 195 -181	-11 36 -45	-11 57 69	-5 105 70	-8 188 197	-5 38 -54
-12 166 160	-7 352 -306	8 98 104	-11 36 -45	-10 39 -34	-9 116 122	-4 132 134	-7 59 63	-4 46 47
-10 391 -360	-6 67 -73		-10 39 -34	-9 88 -77	-9 63 -93	-3 171 -133	-5 167 137	-3 24 30
-9 89 70	-5 34 43		-9 88 -77	-8 230 205	-8 50 53	-2 29 33	-4 202 -219	-2 39 -45
-8 249 227	-4 32 -24	5,4,L	-8 230 205	-7 81 67	-7 118 111	-1 141 118	-3 423 -467	-1 47 -61
-7 91 -72	-3 90 -96		-7 81 67	-6 33 17	-6 68 44	0 25 25	-2 138 89	0 35 45
-6 218 174	-3 90 -96		-6 33 17	-5 277 288	-5 57 58	-2 108 85	-1 75 -73	1 46 -64
-4 203 -171	-2 405 -388	-16 58 -57	-15 29 44					
-3 327 302	-1 209 185	-14 104 87	-14 104 87					
-2 309								

TABLE 2. *The crystallographic coordinates in* $\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Trinitromethide anion 1				
O(11)	^a 1.0245(4)	0.2576(2)	0.2062(2)	1.53(6)
O(12)	0.9407(4)	.2422(2)	.3406(2)	1.71(6)
O(13)	.6213(4)	.1781(2)	.2729(2)	1.54(6)
O(14)	.4573(4)	.3086(2)	.1895(2)	1.67(6)
O(15)	.6052(4)	.4415(2)	.0878(2)	1.64(6)
O(16)	.8842(4)	.4519(2)	.1374(2)	1.48(6)
N(11)	.9157(5)	.2689(3)	.2534(2)	1.33(6)
N(12)	.6019(4)	.2656(3)	.2230(2)	1.22(6)
N(13)	.7460(4)	.4063(2)	.1404(2)	1.17(6)
C(11)	.7503(5)	.3158(3)	.2044(3)	1.28(7)
Trinitromethide anion 2				
O(21)	0.9957(4)	0.6472(2)	0.4666(2)	1.86(6)
O(22)	.7380(4)	.7257(2)	.5074(2)	1.78(6)
O(23)	.8344(4)	.5462(2)	.6584(2)	1.95(6)
O(24)	.6853(4)	.3965(2)	.5992(2)	1.97(6)
O(25)	.6176(4)	.3789(2)	.4040(2)	2.00(6)
O(26)	.6695(4)	.5329(2)	.3300(2)	1.87(6)
N(21)	.8161(4)	.6430(3)	.4892(2)	1.29(6)
N(22)	.7535(5)	.4886(3)	.5871(2)	1.49(6)
N(23)	.6727(5)	.4777(3)	.4057(2)	1.41(6)
C(21)	.7398(6)	.5314(3)	.4946(3)	1.62(7)
Hydrazinium ion 3				
N(31)	0.2074(5)	0.0376(3)	0.3594(3)	1.82(7)
N(32)	.3198(5)	.1121(3)	.3221(2)	1.53(6)
Hydrazinium ion 4				
N(41)	0.0930(5)	0.3367(3)	0.0018(3)	1.53(6)
N(42)	.2647(5)	.3413(3)	-.0125(3)	1.37(6)

^a The values quoted in parentheses are the standard errors in the last digit and were calculated from the final full-matrix least-squares refinement cycle. Average shift/error for last cycle = 0.17 for all parameters except hydrogens.

TABLE 3. *Comparison of hydrogen positions in* $\text{N}_2\text{H}_5^+[\text{C}(\text{NO}_2)_3]^-$

	Weighted difference electron density synthesis			Least squares ^a refinements			Calculation ^b		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
H(1).....	0.189	0.000	0.324	0.187	0.007	0.308	0.180	−0.033	0.315
H(2).....	.139	.084	.367	.156	.075	.385	.093	.080	.359
H(3).....	.349	.076	.281	.358	.075	.281	.365	.070	.269
H(4).....	.386	.140	.365	.397	.143	.368	.424	.136	.380
H(5).....	.256	.160	.293	.253	.169	.289	.250	.183	.292
H(6).....	.088	.392	.043	.091	.382	.069	.076	.404	.045
H(7).....	.101	.269	.034	.086	.267	.033	.078	.261	.036
H(8).....	.349	.330	.041	.337	.328	.044	.354	.324	.054
H(9).....	.306	.290	−.054	.288	.286	−.060	.274	.282	−.065
H(10).....	.285	.416	−.034	.289	.411	−.033	.287	.422	−.036

^a Estimated random standard errors from the least squares refinement are 0.01 in *x*, 0.006 in *y* and 0.005 in *z* (i.e., about 0.13 Å total). The systematic error known to accompany the location by x-ray methods of a covalently bonded hydrogen is 0.1–0.2 Å.

^b Assuming *sp*³ hybridization of N and N—H = 1.03 Å (see text). Ends of N_2H_5^+ ions rotating independently of each other.

TABLE 4. The trinitromethide anion geometries.

Atoms	Distance, Å	Atoms	Angle, deg.
Anion 1			
C(11), N(11)	^a 1.432(5)	N(11), C(11), N(12)	117.3(3)
N(12)	1.397(5)	N(11), C(11), N(13)	118.4(4)
N(13)	1.385(5)	N(12), C(11), N(13)	124.3(3)
N(11), O(11)	1.225(5)	O(11), N(11), O(12)	123.6(3)
O(12)	1.226(4)	O(13), N(12), O(14)	122.0(4)
N(12), O(13)	1.231(4)	O(15), N(13), O(16)	120.4(3)
O(14)	1.228(4)	O(11), N(11), C(11)	118.3(3)
N(13), O(15)	1.238(4)	O(12), N(11), C(11)	118.1(4)
O(16)	1.228(4)	O(13), N(12), C(11)	118.1(3)
O(11), O(12)	2.159(5)	O(14), N(12), C(11)	120.0(3)
O(12), O(13)	2.572(4)	O(15), N(13), C(11)	120.7(3)
O(13), O(14)	2.150(4)	O(16), N(13), C(11)	118.9(3)
O(14), O(15)	2.587(4)		
O(15), O(16)	2.140(4)		
O(16), O(11)	2.618(4)		
Anion 2			
C(21), N(21)	1.456(5)	N(21), C(21), N(22)	116.7(3)
N(22)	1.366(5)	N(21), C(21), N(23)	115.9(3)
N(23)	1.374(5)	N(22), C(21), N(23)	127.2(4)
N(21), O(21)	1.225(5)	O(21), N(21), O(22)	124.3(3)
O(22)	1.214(4)	O(23), N(22), O(24)	121.4(3)
N(22), O(23)	1.239(4)	O(25), N(23), O(26)	123.2(3)
O(24)	1.241(4)	O(21), N(21), C(21)	117.6(3)
N(23), O(25)	1.239(4)	O(22), N(21), C(21)	118.2(4)
O(26)	1.237(4)	O(23), N(22), C(21)	117.3(3)
O(21), O(22)	2.156(5)	O(24), N(22), C(21)	121.3(3)
O(22), O(23)	2.945(4)	O(25), N(23), C(21)	120.1(3)
O(23), O(24)	2.163(4)	O(26), N(23), C(21)	116.8(3)
O(24), O(25)	2.650(4)		
O(25), O(26)	2.178(4)		
O(26), O(21)	2.891(4)		

^a The quantities quoted in parentheses are standard errors based on the standard errors of the positional parameters and the standard errors of the cell dimensions.

group and atoms in neighboring anions of type 1 are O(21) . . . O(12) = 2.92 Å, O(22) . . . O(12) = 2.89 Å, N(21) . . . O(12) = 2.97 Å on one side and O(21) . . . N(21) = 2.93 Å, O(22) . . . N(13) = 2.99 Å on the other side.

Among the differences in the two trinitromethide anions in this structure, the C(11)—N(11) and C(21)—N(21) distances of 1.43 and 1.46 Å, respectively, may reflect in part the decrease in π orbital overlap between C and N since their π orbitals are at 41° and 74° to each other in the two cases. The increased electron density in the remaining C—N π bonds on going from anion 1 to anion 2 is consistent with the shorter distances (table 3) in these bonds in anion 2. Superimposed on this result, however, would be the changes in σ bond length due to differing bond angles and hence different hybridizations of the orbitals in the σ bond skeleton [15]. Further, the N(22) . . . C(21) . . . N(23) angle of 127°

may be at first considered to result from the fact that the N(22) and N(23) nitrogens are almost coplanar (dihedral angles of 5° and 4°) with the C(N)₃ part of the anion 2. However, the shortest intra-ionic inter-nitrogen oxygen-oxygen distance is 2.572 Å for O(12) . . . O(13). If the O(24) . . . O(25) oxygens were this far apart, the N(22) . . . C(21) . . . N(23) angle could decrease by about 2.5°.

Trinitromethide anions and related species have been found in a variety of conformations in crystal structures of other compounds. The following examples show that the conformations these anions assume are very strongly influenced by the environments. The trinitromethide conformations observed in hydrazinium trinitromethide are seen to be plausible when compared with the conformations in the examples.

The trinitromethide anion in Rb⁺[C(NO₂)₃]⁻ has been found in a preliminary study [16] to have an approximately planar C(N)₃ central region, with one NO₂ group twisted about 45° to this central plane, with the oxygens of another NO₂ group above the C(N)₃ plane, and with the oxygens of the third NO₂ group below this plane. In the trinitromethide anion in Cs⁺[C(NO₂)₃]⁻ [16], two of the NO₂ groups have been rotated in opposite directions, one about 75° and the other, 35°. The oxygens of the third NO₂ group are on the same side of the (N)₃ plane as the central C atom.

In Na⁺[C(CN)₃]⁻, the central C atom is 0.024 Å out of the central (C)₄ plane [17]; this is similar to the situation found in anion 2. In K⁺[C(CN)₃]⁻ the corresponding deviation is 0.015 Å. These deviations from planarity have been attributed to the effect of packing in the structure. In K⁺[p(NO₂)C₆H₄C(CN)₂]⁻ the bonding about the central carbon atom is pyramidal and there seems to be some effect of resonance on the aromatic character of the phenyl ring [18].

In K⁺[C(NO₂)₃]⁻, one nitrogens is perpendicular to the rest of the anion [19]. In Ca²⁺[C(C(CN)₂)₃]²⁻·6H₂O, each C(CN)₂ group is rotated out of the plane of the four central carbon atoms by 24° [20]. In a completely planar and symmetrical trinitromethide anion (with distances and angles the averages of those in anion 1) the O . . . O distance between adjacent oxygens in different nitrogens would be 2.42 Å. If the closest permissible approach of these adjacent oxygens is assumed (judging from anion 1) to be about 2.60 Å, the trinitromethide anion cannot be planar and would have to rotate all its nitrogens by about 21° about the C—N bonds to achieve a regular trigonal configuration. This angle is close to the 24° reported in reference 20 for Ca₂²⁺[C(C(CN)₂)₃]²⁻·6H₂O.

4.2. The Hydrazinium Ions

The N—N distances in the hydrazinium ions are N(31)—N(32) = 1.438(6) and N(41)—N(42) = 1.424(7) Å. Possible positions for the hydrogen atoms in the hydrazinium ions were found in the weighted difference synthesis. These positions suggest that the N(31)—N(32) hydrazinium ion is approximately eclipsed and the N(41)—N(42) hydrazinium ion is approximately staggered.

As an independent check on the observed hydrogen positions and in a first-approximation attempt to gain some insight into the hydrazinium conformations found, idealized hydrazinium ions with N—N—H angles of 109.5° (sp^3 hybridization of N), N—H distances of 1.03 Å and N—N distances of 1.431 Å (the average of those quoted above) were first generated in both exactly eclipsed and exactly staggered conformations. The lone pair of electrons in each hydrazinium ion was considered to be on each nitrogen atom in turn. These idealized ions were rotated over 360° in steps of 3° about the N—N vector in an environment of all atoms other than hydrogen which are nearer than 3.5 Å to the nitrogen atoms in the hydrazinium ions. Because of uncertainty in the nature of the hydrogen bond (see for example reference 21), the shortest $H_i \dots X$ distance, D_i , for each hydrogen at each step of the rotation was summed up as

$$\sum_i D_i \quad \text{and} \quad \sum_i 1/D_i$$

to obtain quantities predictive of the hydrazinium orientation. When maximised, $\sum 1/D_i$ is an approximation to the electrostatic term in the hydrogen bonding; it assumes (a) all hydrogens are equally charged, (b) all atoms in the environment are equally charged, (c) there is no electrostatic interaction between hydrogen atoms either within a given ion or in different ions, and (d) the shortest $H_i \dots X$ distance is of overriding importance. Its use involves the reasonable assumption that the electrostatic term is dominant in hydrogen bonding at $H \dots X$ distances of ~ 1.9 Å to ~ 2.4 Å. When minimised, $\sum D_i$ places greater weight on the shortest $H \dots X$ distances, which are known to be the strongest hydrogen bonds.

The hydrogen positions for best hydrogen bonding (according to the $\sum D$ and $\sum 1/D$ criteria) for the *exactly eclipsed* N(31)—N(32) hydrazinium ion with three hydrogen atoms on N(32) were found to agree fairly closely with those observed. For this orientation, $\sum D = 10.437$, $\sum 1/D = 2.403$. The best orientation for the *exactly staggered* form of N(31)—N(32) gave $\sum D = 10.610$ and $\sum 1/D = 2.369$ and thus showed poorer hydrogen bonding to the environment. The form with three hydrogens (the configuration observed in the difference synthesis) on N(32) was able to form better hydrogen bonds than the form with three hydrogens on N(31) according to the $\sum D$ and $\sum 1/D$ criteria. The best hydrogen bonding for the *exactly eclipsed* form of the N(41)—N(42) hydrazinium ion with three hydrogens on N(42) appeared to be close ($\sum D = 10.372$, $\sum 1/D = 2.418$) to that of the *exactly staggered* form ($\sum D = 10.452$, $\sum 1/D = 2.402$). The forms with three hydrogens on N(42) (the configuration observed) were better bonded than those with three hydrogens on N(41).

The *eclipsed* form of the N(41)—N(42) hydrazinium ion has, however, an unreasonably small contact H(7) \dots H(4) = 1.44 Å with the *eclipsed* form of the N(31)—N(32) ion. The *staggered* form of the N(31)—N(32) ion has an unreasonable contact H(1) \dots H(6) = 1.62 Å with the *staggered* form of the N(41)—N(42) ion and an unreasonable contact H(4) \dots

H(7) = 1.53 Å with the *eclipsed* form of N(41)—N(42). Thus, neglecting intra-ionic hydrogen repulsions, the optimum exact conformations seem to be *eclipsed* for N(31)—N(32) and *staggered* for the N(41)—N(42) hydrazinium ions. These conformations are the ones observed. The main difference between predicted staggered and eclipsed forms of the same hydrazinium ion is the location of the hydrogens in the NH_2 group, not those in the NH_3 group.

Since intraionic hydrogen repulsion is highest when the hydrazinium ions are exactly eclipsed and since this repulsion term is apparently low enough to allow the hydrazinium ions to deviate from being exactly staggered, hydrogen positions were then generated by rotating the ends of the ions freely in their environments. The resultant best positions for hydrogens on N(31)—N(32) ($\sum D = 10.390$, $\sum 1/D = 2.413$) agree well (average difference = 0.09 Å) with those calculated for the exactly *eclipsed* form. The best hydrogen positions for H(8), H(9), and H(10) on N(41)—N(42) agree within 0.013 Å with those of the exactly *staggered* form. For the H(6) and H(7) positions, there are two minima, one in the $\sum 1/D$ quantity and one in the $\sum D$ quantity. The resultant conformations of the ions are approximately *staggered* and *eclipsed* respectively. The best H(6) and H(7) positions in the approximately *staggered* form give $\sum D = 10.4496$, $\sum 1/D = 2.4025$ for the whole N(41)—N(42) hydrazinium ion. For the approximately *eclipsed* conformation, the best hydrogen positions give $\sum D = 10.3608$, $\sum 1/D = 2.4205$. To minimize inter-ionic interhydrogen repulsions as stated earlier, the approximately *eclipsed* form of N(31)—N(32) and the approximately *staggered* form of N(41)—N(42) are preferred. These calculated positions for hydrogen are given in table 3 and are the ones used in subsequent calculations. In general, they are near those observed although the positions of those calculated for H(1) and H(2) are slightly different ($\sim .5$ Å) from those observed, but give better hydrogen bonds.

The environments of the hydrazinium ions are shown in figures 4 and 5. The distances in the hydrogen bonds are given in table 5 and are in the normal range. Angles showing the deviation from linearity of the hydrogen bonds are also given in table 5 and are satisfactory. According to Donohue [22] any such angle above 135° is within the normal range for a primary hydrogen bond. From table 5 and figure 3, it may be seen that O(21), O(22) and O(26) in the trinitromethide anions form very weak, if any, hydrogen bonds. The distances to their nearest neighbors (other than hydrogen atoms) in the structure are N(12) \dots O(21) = 2.926(6) Å, N(41) \dots O(22) = 2.899(8) Å, N(13) \dots O(22) = 2.990(5) Å, O(13) \dots O(26) = 2.991(7) Å and N(11) \dots O(26) = 3.020(6) Å. Although none of these neighbors is unusually close, each oxygen not hydrogen bonded is near an NO_2 group and may possibly undergo van der Waals bonding with the π electrons of the NO_2 group.

A. L. Milstead of the Naval Ordnance Station visually estimated the raw intensity data. The x-ray 63

crystallographic computing system [23] was used for all crystallographic computations subsequent to the

calculation of the observed structure factors from the observed data.

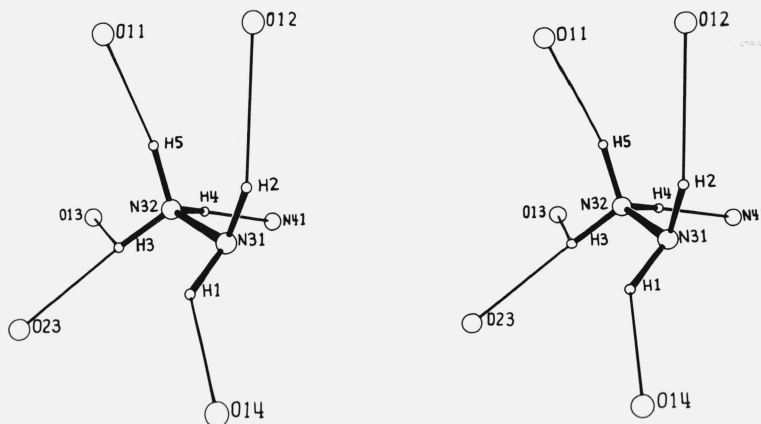


FIGURE 4. The environment of the eclipsed hydrazinium ion N(31)—N(32); atoms within 2.40 Å of the hydrogens are included.

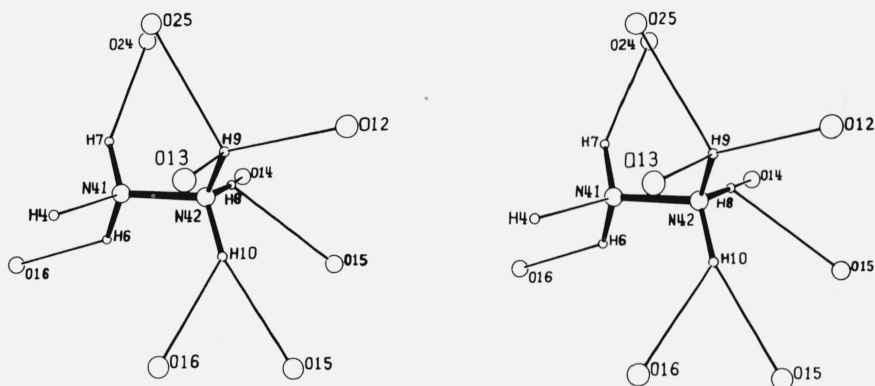


FIGURE 5. The environment of the staggered hydrazinium ion N(41)—N(42); atoms within 2.40 Å of the hydrogens are included.

TABLE 5. Possible hydrogen bonds in $\text{N}_2\text{H}_5^+ [\text{C}(\text{NO}_2)_3]^-$

	$\text{H}_R \dots \text{X}, \text{\AA}$	$\text{H}_D \dots \text{X}, \text{\AA}$	$\text{H}_C \dots \text{X}, \text{\AA}$	N—H ... X angle		
				R, deg	D, deg	C, deg
H(1), O(14).....	2.6	2.5	2.15	113	132	138
H(2), O(12).....	2.6	2.4	2.24	138	162	149
H(3), O(23).....	2.2	2.2	2.03	154	160	152
O(13).....	2.4	2.5	2.39	103	105	100
O(16).....	2.5	2.6	> 2.4	112	109
O(24).....	2.6	2.6	> 2.4	115	119
H(4), N(41).....	2.1	2.2	1.91	160	162	169
O(13).....	2.5	2.6	> 2.4	98	97
H(5), O(11).....	2.1	2.2	2.06	160	165	151
H(6), O(16).....	2.3	2.4	2.30	115	136	136
N(31).....	2.5	2.5	> 2.4	136	137
H(7), O(24).....	2.2	2.2	2.14	155	164	149
O(22).....	2.5	2.6	> 2.4	104	97
O(25).....	2.5	2.5	> 2.4	103	105
H(8), O(14).....	2.0	2.0	1.87	166	156	162
O(15).....	2.4	2.4	2.37	118	124	114
H(9), O(12).....	2.1	2.1	2.11	142	151	135
O(25).....	2.3	2.5	2.33	120	112	125
O(13).....	2.4	2.5	2.25	113	107	116
H(10), O(15).....	2.1	2.1	2.04	168	164	163
O(16).....	2.4	2.3	2.25	132	134	133

^a Refers to hydrogen positions from least squares refinements.^b Refers to hydrogen positions from difference synthesis.^c Refers to hydrogen positions from calculation (see text).

5. References

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